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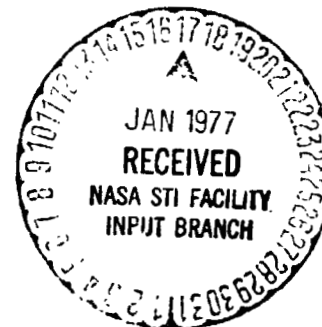
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DEVELOPMENT OF TECHNIQUES FOR PROCESSING  
METAL-METAL OXIDE SYSTEMS

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16. ABSTRACT  <p>This report describes the results of investigations to develop techniques for producing model metal-metal oxide systems for the purpose of evaluating the results of processing such systems in the low-gravity environment afforded by a drop tower facility. Because of the lack of success in producing suitable materials samples and techniques for processing in the 3.5 seconds available, the program was discontinued.</p>			
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## FOREWORD

This report was prepared by Arthur D. Little, Inc., Cambridge, Massachusetts, and is a summary of the efforts during the period 24 October 1972 to 30 September 1973 under Contract No. NAS8-29145, "Development of Techniques for Processing Metal-Metal Oxide Systems." It assembles in a single document the results of the program which have been presented orally during meetings with the COR at NASA/MSFC and by means of the Monthly Progress Reports. The report is the Final (Phase 1) Report required under the terms of the contract and served as the basis for a decision by the Government to reject Phases 2 and 3 of the program.

It has been the objective of efforts under Phase 1 of this program to develop techniques for producing model metal-metal oxide systems for the purpose of evaluating the results of processing such systems in a low gravity environment. This has included the selection of materials properties such as wettability, density difference and sample processing techniques on the matrix structure and oxide distribution of a metal-metal oxide system. It has been a further objective of Phase 1 to consider and propose an experiment for studying the effects of processing such systems in a low gravity environment in the appropriate low-g test facility.

The objectives of Phases 2 and 3 of the program, as stated in Modification No. 2 to Contract No. NAS8-29145 were:

- Phase 2: To design ampoules required for the proposed experiment; to provide the metal-metal oxide samples for processing in MSFC low gravity facilities; and to evaluate the results by comparison of the samples processed in low gravity with identical samples processed under low-g conditions.
- Phase 3: To define follow-on experiments for future opportunities in sounding rockets, a Skylab-type facility, shuttle sortie mission, etc.

The program was originated and managed by the George C. Marshall Space Flight Center under the technical direction of Mr. I. C. Yates.

The work performed by the Materials Section of the Physical Sciences Group, with Mr. Philip C. Johnson as Principal Investigator. The technical personnel who supported this program are:

- Dr. John S. Haggerty, Materials Section
- Dr. D. William Lee, Section Leader, Materials Section
- Dr. John L. O'Brien, Materials Section
- Dr. Edward T. Peters, Materials Section
- Mr. Michael Rossetti, Materials Section

The advice of Prof. Donald R. Uhlmann of the Massachusetts Institute of Technology is gratefully acknowledged for discussions relating to the interactions between particles and a solid-liquid interface.

## I. INTRODUCTION

The weightless environment of space flight offers an opportunity to produce unique materials. One type of process which appears particularly attractive is the solidification of materials from a fully liquid state or from a mixed solid-liquid system. The important factors which can be considered unique to a low gravity process are: 1) absence of gravity segregation of components having different densities, 2) elimination of convective effects in the liquid due to composition or thermal density differences in a liquid and 3) increased prominence of surface tension effects.

Materials which are particularly promising in terms of low gravity processing are multiphase materials in which there are significant differences in density between the phases. This program is based on the development of a model of a specific type of such multiphase material--a dispersion of metal oxides in a metal matrix, representative of higher melting point composite materials of technological importance. The materials systems is not intended to model those that depend on a solid state transformation, for example, to impart a dispersion of one phase within a matrix of a second phase, but rather, are materials in which ideally one phase goes through the solid-liquid-solid phase transformations while the other remains a solid throughout the processing procedure. The particular solid phase that is present may vary in chemistry, size, morphology, volume fraction and interaction with the matrix, depending on the specific materials system. Some typical examples of technical materials of this sort, which can span the range of second phase particle size, include: 1) metal-metal oxide materials, such as dispersion strengthened alloys and the various SAP materials, 2) whisker, fiber and particulate reinforced metals, 3) cemented carbides, 4) a wide range of multiphase systems which are exemplified by friction and bearing materials, and 5) dispersed nuclear fuel and control rod materials.

The processing of these materials are significantly limited and affected by gravity-induced effects that accompany processing. Typically, these materials must now be produced by powder metallurgy techniques in which the liquid phase is never present or is limited to very small volume fractions (such as in liquid-phase-sintering). Powder metallurgy techniques are not immune to gravity-induced effects, such as phase segregation, even under best practice of the technology. Powder metallurgy inherently poses processing difficulties such as oxidation of the intended ductile or matrix powders and residual porosity in the final product. Low gravity processing offers the opportunity for controlled dispersion of a solid metal oxide phase in a metal matrix by melting and solidification of the metal phase to a fully dense composite material.

## II. SUMMARY-PHASE 1 EXPERIMENTAL PROGRAM AND RESULTS

### A. Introduction

The primary impetus for the program, "Development of Techniques for Processing Metal-Metal Oxide Systems" as originally proposed by Arthur D. Little, Inc., was the results of a series of experiments performed on the Apollo 14 mission during the translunar and transearth coast periods.<sup>(1)</sup> These involved melting and solidification of three general types of materials systems:

- Precompressed powder compacts containing dispersed particles
- Matrix material with fibers, particles, whiskers and/or gas
- Immiscible materials dispersions.

Arthur D. Little, Inc., contributed to the planning of these experiments and performed the characterization of three of the flight and control samples.<sup>(2)</sup>

There was a total of 18 samples prepared for processing during the Apollo 14 mission, of which only 11 were processed because of time constraints. In general, post-examination of these samples and their earth-processed controls indicated that

- Enhanced dispersion and distribution of the fibers, particles and gases in the matrix were found in the space processed samples.
- Normally immiscible mixtures showed stable dispersions unattainable on earth.

Additional particle-dispersed specimens were prepared for the Apollo 15 mission, but were cancelled. These included W spheres and B<sub>4</sub>C particles, at two loading percentages each, in precompressed In-Bi eutectic powders.

These samples were subsequently kept in the liquid state over long periods of time on earth in order to investigate 1-g segregation effects. The expected segregation effects were not observed. It was postulated that particle motion in the liquid was impeded by lack of wetting, perhaps due to the presence of a gas film on the particles.

While the low gravity composite melting experiments on the Apollo 14 mission showed that unique materials in terms of improved dispersions of second phases could be produced, many more questions were raised by the results. Some of these can be traced to the inability to perfect the procedures for preparing materials and experimental systems because of the short time between authorization of the experiments and delivery of the flight-qualified experiment hardware package to the Kennedy Space Center. Some of the more prevalent difficulties were:

1. Lack of Consistency of Point of Heat Removal. To some extent, the melts were in a free-float condition within the capsules, so that heat was removed more or less at random places as opposed to one end (as required for directional solidification). This made it difficult to reconstruct the solidification sequence.

2. Change in Volume on Freezing. Coupled with the lack of control of freezing direction, shrinkage of the metal in the metal matrix samples resulted in internal shrinkage porosity. While in general this porosity could be distinguished from argon gas porosity, it made evaluation of the gas dispersion difficult.

3. Non-wettability of the Particles and Fibers. In many instances, the dispersed particles and fibers appeared not to have been wetted by the melt. The combination of lack of controlled solidification direction and the presence of shrinkage porosity thus resulted in a redistribution of many of the particles and fibers to the shrinkage pores and to external surfaces which were the last to freeze.

It was believed at the outset of this program that control of heat removal or solidification parameters and compensation for change in volume on shrinkage were the lesser of the problems to be overcome in the development of an experimental package for meaningful low gravity experiments, irregardless of the specific experimental facility and time frame which might be eventually used for the Phase 2 experiments. These are problems which can basically be solved by proper design of the ampoule and the means of heating and cooling. Concurrent with this program, hardware was being developed under other NASA/MSFC contracts which could be adapted to meet the requirements for small metal-metal oxide materials systems, once those systems had been developed by the TRW Systems Group for the production of homogenized alloys of immiscible metals was considered jointly with the NASA/MSFC COR, and it was agreed that this hardware, with minimal modification, could be adopted to provide a meaningful low gravity experiment for the drop tower facility.<sup>(3)</sup> Similarly, experimental packages could be defined for longer time frame low gravity experiments such as sounding rocket flights and orbital missions.

For the purposes of this program, it was concluded that the drop tower facilities would be used for the low gravity experiments, and with the agreement of NASA/MSFC under Modification No. 2 to Contract No. NAS8-29145, that Arthur D. Little, Inc., would supply the design of the ampoule and six metal-metal oxide samples for the purposes described under Phase 2. Actual fabrication of the ampoules and the remainder of the experimental package, such as ampoules, containers, furnaces and quenching mechanism, would be provided by the Government.

The primary objective of Phase 1 of this program has been the investigation of the metal-metal oxide materials systems themselves. The primary criteria, based on the conclusions reached by the Apollo 14 and 15 investigation, have been:



- Wettability of the metal oxide by the metal matrix in the liquid state
- Incorporability of the metal oxide into a matrix system which will undergo a solid-liquid-solid phase transformation sequence under low gravity conditions.

It was recognized at the outset of this program that wetting of a metal oxide by a liquid metal is not a trivial problem. The technology developed in, for example, the areas of soldering and brazing is largely concerned with the uses of fluxes, controlled atmospheres, or other means to remove oxides from metal surfaces in order to obtain a bond between a solid object (or metal particle covered with its oxide) and a liquid solder or braze (or metal matrix which at some point in processing is in the form of a liquid). For the purposes of a metal-metal oxide materials system, this approach naturally suggests a sacrificial metal coating on the metal oxide phase which can be fluxed and/or otherwise treated to obtain wetting by the liquid matrix. The key drawback in such systems is that the coatings are usually sacrificial, and put extreme constraints on subsequent low gravity processing. Sacrificial coatings alter the metal matrix composition, and in the extreme, may be completely scavenged from the surface of the oxide and result in dewetting. Coatings were employed for this purpose on the particulate species in many of the Apollo 14 experiments. The post-flight examination of these samples indicated that either the particles were not wet by the liquid matrix in the first instance, that they wet and subsequently dewet, or that they were not incorporated into the solid interface during growth for other reasons entirely. The emphasis during the Phase 1 investigations in this program has been on directly wetting metal-metal oxide systems. Because of some degree of success achieved with these systems, coatings have not been investigated in this program, although this option clearly remains open as a means of obtaining initial wetting of the oxide particles in metal-metal oxide systems. The kinetics of melt contamination and dewetting of the particles due to complete dissolution of the coatings would have to be carefully investigated for any proposed low gravity experiments employing coatings to achieve initial wetting of the particles.

With the emphasis on directly wetting systems, the technology and literature for joining glasses and ceramics directly by means of molten metals has been more appropriate background for the work conducted in this program. However, this technology and literature are both quite limited in terms of a detailed understanding of the mechanisms whereby certain metals wet oxides, the techniques required to obtain this wetting, and, in fact, what the term "wetting" actually means in such systems. In this program, conventional criteria have been used. That is, the ability to form low-contact-angle coatings of the matrix alloys on the bulk oxides and on oxide particles, without the occurrence of dewetting upon remelting of the alloy, has been considered to be primary evidence

of wetting in the conventional sense. The technology and literature on glass and ceramic sealing by molten metals, though meagre, has therefore been used as a guide to the Phase 1 efforts.

The importance of the second primary Phase 1 criterion listed above--the incorporability of the metal oxide into an advancing solidification interface--has become increasingly recognized during the Phase 1 efforts. There was much evidence in the Phase 1 investigations that oxide particles were being wet but that they were being rejected by advancing solidification interfaces. A detailed examination of this phenomenon was considered to be beyond the scope of this program. Clearly, foreign particles, including metal oxides, are very often incorporated into cast metal ingots, even though their presence in this instance is generally regarded as undesirable. In a related NASA/MSFC-funded program, General Dynamics has successfully incorporated foreign particulate materials into metal matrices.<sup>(4)</sup> Some literature exists on the interaction between particles and solid-liquid interfaces, much of it theoretical, and almost entirely devoted to particles in organic or ice matrices under growth conditions far removed from those contemplated for near-term low gravity experiments.<sup>(5-7)</sup> Nevertheless, particle rejection at growth interfaces does occur and is believed to have been observed in some experiments performed in this program on metal-metal oxide systems. Therefore, an increasing awareness of the particle-rejection phenomenon has developed during the course of these investigations, and must be considered at least on a practical basis in the design of a specific low gravity experiment involving metal processing of metal-metal oxide systems.

## B. Selection of Materials

1. Metal Matrix Alloys. The materials for the metal-metal oxide system were initially selected largely on the basis of literature dealing with joining and sealing of non-metal materials by metals. This literature is largely reviewed in two references, Manko<sup>(8)</sup> and Kohl.<sup>(9)</sup> Several of the producers of low-melting point alloys intended for use with non-metallic solids were also consulted, but very little helpful information was obtained, either with respect to the optimum materials or to techniques for enhancing wettability of the oxides.

The criteria for selection were:

- Potential wettability of oxides by the metal
- Low melting point. An upper limit was placed at that of pure aluminum (660°C).
- Specific gravity compatible with both high (greater than 1.5) and low ratios between the metal and readily available metal oxides.
- Low toxicity
- Low vapor pressure
- Chemical and physical compatibility of the metal, the oxide and candidate capsule materials.

- Readily available or producible in the Arthur D. Little, Inc., laboratories.

The metal matrix materials actually selected and evaluated to varying extents are listed below in Table I.

TABLE I

	<u>Density (gm/cc)</u>	<u>Melting Point (°C)</u>
60Sn-40Pb	8.6	182.2-290.6
90In-10Ag	8.1	141.0-237.5
50In-50Pb	9.1	180-208.9
Indium	7.3	156.7 (M.P.)
50In-50Sn	7.7	117-125

Sources: Ref. 8 and 10

It should be noted that the 60Sn-40Pb alloy was not intended to serve as a matrix material for the metal-metal oxide systems, except under circumstances where non-wetting of the oxide was or might be desired. Its primary purpose was for use with particulate copper under mild fluxed conditions to evaluate experimental apparatus and procedures with a system in which wetting is assured.

2. Metal Oxide Materials. Both alumina ( $Al_2O_3$ ) and silica ( $SiO_2$ ) were originally selected as candidate metal oxide materials for investigation in this program. Both have low densities. During the program, experimental work was performed on three types of materials:

- Commercial purity 80 mesh  $Al_2O_3$  grit obtained from the Norton Company
- High density, high purity  $Al_2O_3$  monolithic shapes or Degussit Grade Al23 obtained from Degussa, Inc. This material has a very high density (3.7-3.9 gm/cc) and purity (>99.5%  $Al_2O_3$ ) as quoted by the supplier. Typical impurities, determined independently by Arthur D. Little, Inc., are, in weight percent, 0.1  $SiO_2$ , .05  $Fe_2O_3$ , 0.2  $MgO$ , 0.05  $CaO$  and 0.20  $Na_2O$ . In some instances, this material was ball milled to obtain experimental quantities of high purity  $Al_2O_3$  powder.
- Pyrex glass, either in monolithic shapes or as graded powders produced by ball milling and screening of Pyrex slides. Pyrex is the proprietary trademark for Corning Glass No. 7740. It is a low alkali content borosilicate glass, free from magnesia-lime-zinc group elements, heavy metals, antimony and arsenic.

The major constituents in Pyrex are approximately 80% SiO<sub>2</sub>, 12%B<sub>2</sub>O<sub>3</sub>, 3%Al<sub>2</sub>O<sub>3</sub> and 4%Na<sub>2</sub>O. Its density is 2.23 gm/cc and has a strain point of approximately 515°C and a softening point of approximately 820°C.

At a later stage in the Phase I program, it was decided that, once the techniques for producing composites using Al<sub>2</sub>O<sub>3</sub> and Pyrex had been developed, some solidification experiments would be carried out using oxides having densities similar to those of the metal matrices.

These experiments have not been performed, but a list of candidate metal oxides was generated.

TABLE II

	<u>Density (gm/cc)</u>	<u>Melting Point (°C)</u>
Ac <sub>2</sub> O <sub>3</sub>	9.19	----
CeO <sub>2</sub>	7.132	2600
Dy <sub>2</sub> O <sub>3</sub>	7.81	2340
Eu <sub>2</sub> O <sub>3</sub>	7.42	2050
Ge <sub>2</sub> O <sub>3</sub>	7.407	2350
In <sub>2</sub> O <sub>3</sub>	7.179	
Ta <sub>2</sub> O <sub>3</sub>	8.2	1800
ThO <sub>2</sub>	9.86	3050
WO <sub>3</sub>	7.16	1473
UO <sub>2</sub>	10.96	2500

Sources: Ref. 11 and 12

### C. Metal-Metal Oxide System Experiments

1. Introduction. Two basic approaches to the preparation of metal-metal oxide samples were considered as possibilities for the program.

- Cold, hot or isostatic pressing of premixed powders of the metal and the metal oxide, without melting of the matrix alloy prior to the low gravity experiments.
- Preparation of samples by incorporation of the metal oxide solid particles into the molten matrix metal in the earth laboratory.

The latter approach, melt processing, clearly has some disadvantages. Chief among them is gravity segregation of the samples in the earth laboratory. However, it was believed that there were ways to overcome this problem. The simplest approach would involve fast quenching of a sample in which the oxide particles were dispersed by mixing prior to the quench. In the earth laboratory, there would be obvious limitations on the size of a sample which could be prepared in this way, depending primarily on the metal-metal oxide density ratio and on the particle size and configuration. An alternative approach which was considered would be feeding of the components into the sample as it is being solidified unidirectionally in a vertical position.

Melt processing, however, seemed the best of the two approaches for a number of reasons. It was anticipated that special procedures might be required to obtain wetting of the metal oxide particles, and that such wetting should be accomplished in the sample prior to low gravity experiments. Moreover, some of the results of the Apollo 14 experiments suggested that processing of the sample by powder metallurgy techniques might lead to problems associated with remnant oxides on the metal matrix powders which would remain solid during the low gravity experiments. These oxide skins could impede motion of both the liquid and the metal oxide particles and thus provide meaningless, less useful, or misleading results.

2. Materials Preparation. As has been noted, literature dealing with the wetting of both crystalline and glass metal oxides is limited, and the literature on joining and sealing was found to be the most helpful.(8,9) Additional information is provided by Belser(13) and McGuire(14) Based on this literature, the three basic criteria are:

- Conventional fluxes do not promote wetting and, in fact, inhibit it, and their presence must be carefully avoided.
- The metal oxides must be thoroughly cleaned with an emphasis on treatment in highly oxidizing solutions followed by bake-out at 350°C or higher.
- Mechanical abrasion of the molten alloy against the metal oxide serves to form an adherent bond between the two.

The bulk of the work in Phase 1 of this program has been directed towards development of the optimum materials treatment prior to melt processing, and the investigation of a number of ways in which metal oxide powders could be incorporated into the melt in the presence of sufficient mechanical agitation to promote wetting of the powders.

The undesirability of conventional fluxes was established early in the program. Several fluxes of the rosin type were used with several of the indium alloys and both alumina and Pyrex oxides. In all cases, the fluxes acted as a barrier to prevent adhesion. On tests with copper metal shot, the fluxes did perform their function, removing the copper and alloy oxides and resulting in good wetting by the indium alloys.

The procedure which was eventually adopted for treating the metal oxides is outlined below:

- a. Ultrasonic cleaning in a boiling solution of 10 grams of NaOH plus a few drops of commercial wetting agent in 100 ml of deionized water, followed by ultrasonic rinsing in deionized water.
- b. Ultrasonic cleaning in a boiling solution of 5 grams of  $\text{KMnO}_4$  in 100 ml of the deionized water, followed by ultrasonic rinsing in deionized water.
- c. Ultrasonic cleaning in a boiling 20% solution of  $\text{H}_2\text{O}_2$  in deionized water, with several drops of ammonium hydroxide to adjust the pH to 11, followed by ultrasonic rinsing in deionized water, and isopropyl alcohol. The powder is stored in the isopropyl alcohol until ready for use. The alcohol is then decanted and the powder dried and baked at 325-350°C.

In one experiment, Pyrex powder was further prepared by baking under a vacuum of  $5 \times 10^{-5}$  mm of Hg. The powder was contained in a Pyrex beaker on a graphite support which also functioned as a susceptor for RF heating. While there was no means for temperature measurement, baking was accomplished by turning the power on and off at a level which would just cause the susceptor to radiate visibly. While the subsequent attempts to incorporate the powder into 50In-50Pb were not successful, it is believed that failure was due to insufficient agitation of the melt, and that vacuum baking of the powders is probably a useful stage of powder pretreatment.

The alloys and all metal components for the various experiments were ultrasonically degreased in trichloroethene, methyl alcohol and briefly in a 5% nitral solution. They were then stored in isopropyl alcohol until ready for use.

### 3. Preliminary Wetting Tests

a) Preliminary wetting tests were performed on monolithic shapes of  $\text{Al}_2\text{O}_3$  and Pyrex glass using the alloys listed in Figure 1. The metal oxide shapes were preheated in air to a temperature approximately 100°C above the liquidus temperature of the metal or alloy. The alloys were applied to the substrates with and without abrasion with a heated stainless steel tool. Without abrasion, indium, 90In-10Ag, 50In-50Sn, and 50In-50Pb were applied by this method. The samples on the left were applied without abrasion, those on the right with abrasion. Two preheated Pyrex slides can be firmly joined by pressing a piece of the indium alloys between them.

60 Sn-40Pb

50 In-50 Sn

50 In-50 Pb



FIGURE 1 Three Alloys Applied to Monolithic  $Al_2O_3$ .  
Samples on the Right Wiped on With a Hot  
Stainless Steel Spatula

Pure indium is very soft, and characterization procedures were thus anticipated to pose problems. Also, the 90In-10Ag did show some tendency to dewet on reheating. Further work on the program was therefore performed using the 50In-50Sn and 50In-50Pb alloys. These appeared to behave similarly in all subsequent investigations.

b) Manual mixing of metal-metal oxide melts - Much of the work in this program intended to wet metal oxide powders and to prepare samples for earth laboratory experiments utilized simple manually mixing of the prepared  $Al_2O_3$  and Pyrex powders and indium alloys. A small, simple resistance furnace was constructed for heating small samples in Pyrex beakers or other containers. Provision was made for temperature measurement, introduction of controlled atmospheres, and viewing through the front of the furnace, which was a piece of Pyrex plate.

Without any mixing or abrasion of the metal oxide powders in the alloy melt, no wetting could be achieved. However, by simple stirring, the oxides in various forms could be incorporated into the metal matrix. This manual mixing technique, using 5 ml Pyrex beakers, was used primarily during the development of the materials preparation procedures described above. Figure 2a illustrates a sample of 50In-50Pb prepared in this manner, with 80 mesh  $Al_2O_3$  powder segregated towards the top of the sample due to gravity. Figure 2b is a similar sample, except that it also contains a piece of monolithic  $Al_2O_3$  rod. The flow of the matrix around the rod seems to indicate wetting. The sample in Figure 2b also has a portion of the Pyrex beaker still attached to the bottom. There is excellent adhesion; these samples were prepared for examination by breaking off as much of the beaker with a hammer and then sectioning with a diamond saw. Similar results have been obtained with monolithic Pyrex pieces and Pyrex as small as 80 mesh. Attempts to incorporate smaller particles were not successful. It is believed that the smaller particles had layers of surface moisture or gas despite baking which prevented wetting. Manual mixing with +200 -80 mesh Pyrex powders resulted in a mixed dross of the powders and the oxides of the metal matrix alloy.

c) Ultrasonic mixing - It was proposed that the introduction of ultrasonic energy into the mixed metal-metal oxide melt might be a means for successful incorporation of finer powders into the matrices. However, investigation of the equipment available at Arthur D. Little, Inc., and discussions both internally and with the ultrasonic equipment vendors indicated that this equipment was not suitable for the intended purpose. It had been proposed that an ultrasonically driven tip be immersed directly into the mixed melt. The problems that were foreseen using this approach were 1) the need to preheat the horn to melt temperatures and yet maintain the transducer temperature at essentially room temperature, with the horn acting as a very large heat sink, 2) the need to immerse the horn tip at least 1.5 cm into the melt to avoid flexural failure of the tip, 3) rapid erosion of the horn by the oxides and 4) cavitation of the melt at the oxide particle surfaces, possibly resulting in undesirable creation and entrapment of voids.





FIGURE 2a Sample N34 80 Mesh  $\text{Al}_2\text{O}_3$   
Powder Manually Incorporated into 50In-50Pb 5.7x



FIGURE 2b Sample N19 80 Mesh  $\text{Al}_2\text{O}_3$  Powder and 1/8  
Inch  $\text{Al}_2\text{O}_3$  Rod Manually Incorporated into  
50In-50Pb 5.7x

It is still believed that ultrasonic energy might prove to be a useful approach to preparation of the metal-metal oxide systems. However, the equipment should be similar to that sold commercially which is specifically designed for ultrasonic soldering. An acoustic mixer such as that developed by the TRW Systems Group might also provide sufficient energy, both for ground preparation of samples and for low gravity experiments.(15)

d) Electromagnetic processing - Several attempts were made to utilize electromagnetic coupling directly to the metal matrix to perform the dual functions of heating and mixing. Metal-metal oxide systems were loaded into 5 ml Pyrex beakers and placed in the coil of a 450 KHz generator without a susceptor. Melting was accomplished very quickly, but this frequency is too high to cause significant stirring. It is possible that a lower frequency (below 10 KHz) might provide sufficient agitation to promote wetting as well as provide a uniform dispersion of the oxide in the matrix.

e) Mechanical coating - There was some evidence developed during the program that the mechanism of wetting might involve wetting of the metal matrix to its own oxide. Mixtures of Pyrex powder and indium alloys were processed in a ball mill in the solid state. The powders were coated with what appeared to be the metals and their oxides. However, subsequent efforts to incorporate these coated powders into the molten metals by manual mixing were unsuccessful.

4. Metal-Metal Oxide Systems Prepared by Mechanical Agitation. Based on the preliminary wetting tests, it was concluded that agitation of the melts was required which was somewhat more vigorous than that provided by manual mixing. The materials preparation techniques were still in development, and success with manual mixing was sporadic.

A triple container was fabricated for evaluation of techniques for obtaining mechanical agitation by means other than stirring. This consists of a 321 stainless steel sleeve 6.35 mm (1/4 inch) inside diameter by 25.5 mm (1 inch) long sample capsule which fits inside a second container. These are then heated to the desired temperature. The final outside container is adaptable to a variety of mixing equipment, including a paint mixer, a pneumatic vibrator, ball-mills and indirect ultrasonic vibration. The heated container containing the sleeve and the sample is inserted into the cold adapter containers on the mixing equipment.

Initial tests with this system indicated that the thermal inertia balance between the heated inner containers and the cold outer container was marginal in terms of the mixing time which could be obtained before the onset of solidification. Nevertheless, several successful samples were made using 60Sn-40Pb solder with copper shot as a model system. Similar attempts using the metal-metal oxide systems were unsuccessful, and attention was then refocused on materials preparation techniques, manual mixing of samples in beakers, and preparation of samples in the inner portion of the shaker assembly by manually agitating the heated container without inserting the hot container into the cold adapters for the various

mixing equipment. Subsequent success with the metal sample capsule, particularly when a small tungsten pestle was included in the metal-metal oxide mix, suggests that mechanical agitation may nevertheless be a promising processing approach. This would require minimum redesign or modification of the assembly to provide a better heat balance between the hot and cold containers to permit longer mixing times.

5. Metal-Metal Oxide Systems and Experiments Prepared by the Various Techniques. As the techniques for materials preparation, particularly that of the oxide powders were established, successful sample materials were produced by three techniques.

- Manual mixing of the metal-metal oxide melt followed by solidification in the beaker with attempts made to control the direction of solidification upwards or downwards.
- Manual mixing of the metal-metal oxide melt followed by chill casting into a graphite mold.
- Manual agitation of the heated steel sample container, again with attempts to control the solidification conditions.

a) A 50In-50Pb sample was prepared containing a relatively large volume fraction of +80 -60 Pyrex powder by manual mixing in the beaker, followed by solidification by placing the beaker on a cold brass heat sink. A section of the sample indicated that a high density of oxide powders had been incorporated and segregated at the top. The sample was then inverted 180° in a beaker and remelted and again solidified on a cold brass plate. The Pyrex did not segregate vertically due to gravity forces as expected. The experiment was repeated with the same results. The structure after the second inverted melt is shown in Figure 3a. The sample has conformed to the curvature of the beaker bottom. There is apparently either some bridging between the particles at these high volume loadings or the matrix is high in matrix oxide in this region, so that movement of the particles is prevented. The etched microstructure at higher magnification Figure 3b suggests possible bridging of the Pyrex particles, but does not indicate excessive matrix oxide present.

It was postulated that the expected gravity segregation might be observed at lower volume fractions of the metal oxide. Two samples were prepared by manual mixing followed by chill casting into a graphite mold, one with +80 -60 mesh Pyrex and one with +60 -35 Pyrex. Both had 50In-50Pb matrices. In both cases, a fairly low density segregation of particles occurred at the top of the sample, as indicated by the +80 -60 sample shown in Figure 4, Sample N43. (The whole width of the sample is not visible due to the microscope support ring.) The sample containing the +60 -35 mesh Pyrex was inverted in a beaker, remelted, then solidified fairly rapidly by partial immersion of the beaker in water. The beaker cracked and "danced" around in the water pool, causing a significant amount of melt agitation. Water vaporized to form a gas

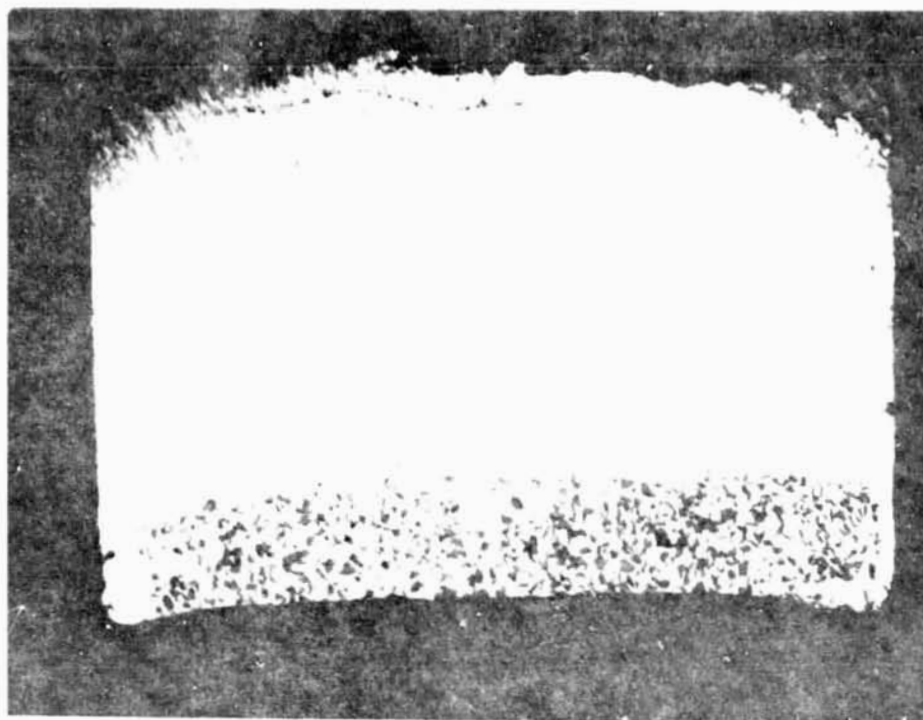


FIGURE 3a Sample N37-2 Pyrex in 50In-50Pb  
After Double Melting in the Inverted  
Position 5.7x

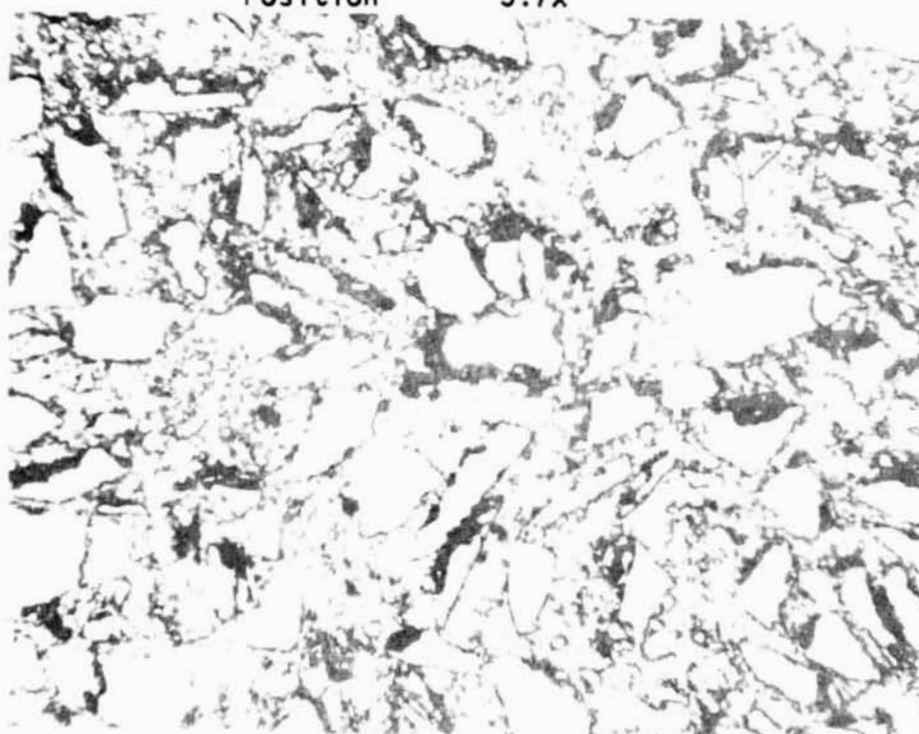


FIGURE 3b Sample N37-2 at Higher Magnification. Small  
White Inclusions are Embedded Polishing Media 62.5x



FIGURE 4 Sample N43 Pyrex Powder Incorporated  
Into 50In-50Pb by Manually Mixing and  
Chill Casting 7x

void at the bottom of the sample, but the Pyrex particles in this case reseggregated to the new top of the sample, Figure 5a (Sample N41-2). It should be noted that the oxide particles also tended to segregate towards the center of the top of the sample, a possible indication of rejection of the particles at the interface growing in from the side of the sample.

The second sample (+80 -60 mesh Pyrex) was also inverted, remelted and solidified more slowly on a copper heat sink (Figure 5b, Sample N43-2). In this case, there was no agitation; some of the oxide reseggregated to the top while much of it remained at the bottom. Also, under these slow solidification conditions, some of the Pyrex was observed to be located on the top surface of the sample. This again may be an indication of particle rejection by the solidification interface.

b) It has also been possible to process metal-metal oxide samples in the metal capsule under certain conditions. The most successful sample is typified by Sample N47, Figure 6. This required careful preparation of the materials as detailed in Section II-C-2, loading the 2.54 cm (1 inch) long sample sleeve to no more than one-half of its total volume, and the inclusion of a small piece of tungsten to act as a pestle. The capsule was heated, manually agitated and water quenched. Despite the rapid quench, the +80 -60 mesh Pyrex all segregated to the top of the sample. The tungsten, of course, segregated to the bottom and, somewhat surprisingly, was not wet by the matrix (50In-50Pb). The tungsten is not visible in Figure 6.

c) Sample N33, Figure 7, illustrates many of the problems that have been encountered in processing metal-metal oxide systems. The matrix in this case was 50In-50Sn with +60 -35 mesh Pyrex powders. The mixture was about 20 v/o powder, but the capsule sleeve was only about one-half filled. No tungsten pestle was used. The powder was loaded at the top of the alloy slug and melted in that position. After reaching approximately 100°C superheat, the capsule was manually agitated and inverted on the brass heat sink. Referring to Figure 7, very little of the oxide has been incorporated into the matrix. Several pieces are trapped between the matrix and the stainless steel sample sleeve. Most of the particles have reseggregated under gravity to the top of the sample as expected. However, some of them appear to have been pushed ahead of the matrix solidification front and are only weakly adhered to the new top surface. In this instance, white Pyrex powders fell out of the capsule--a common occurrence during the early part of these investigations and an indication that the powders were never wet by the matrix in the first place.

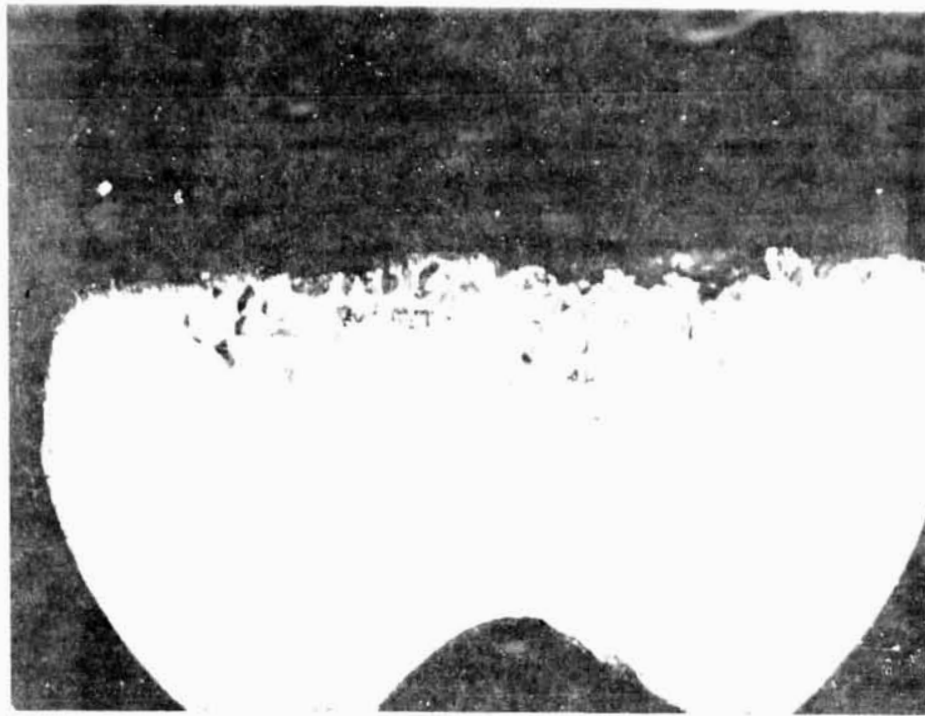


FIGURE 5a Sample N41-2 Pyrex Powder in 50In-50Pb. Sample  
Inverted and Solidified with Agitation 7x

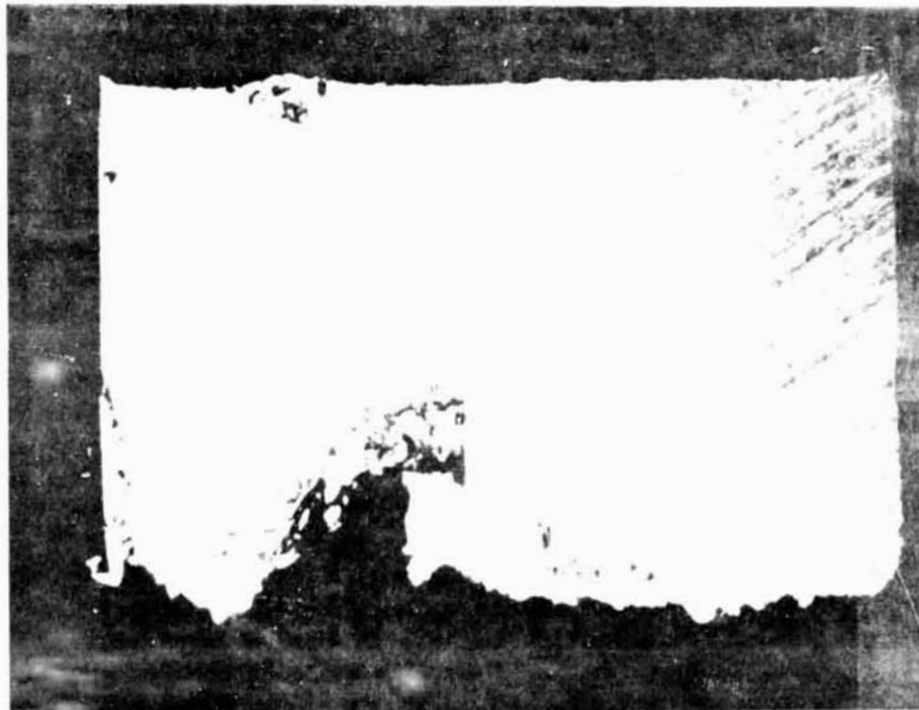


Figure 5b Sample N43-2 Pyrex Powder in 50In-50Pb.  
Sample Inverted and Solidified without  
Agitation 5.7x

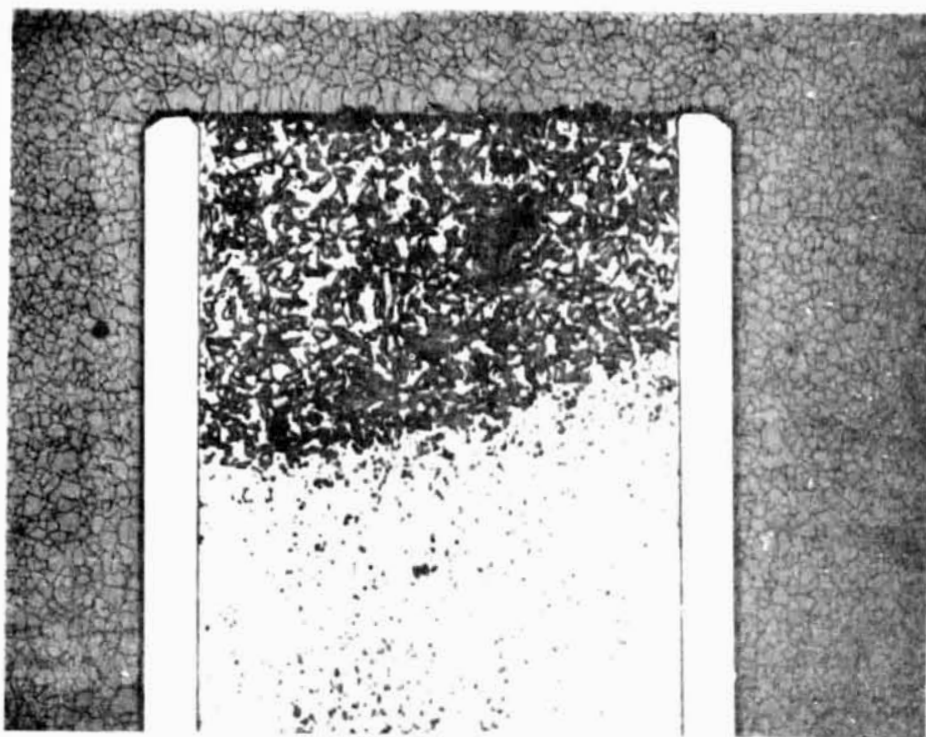


FIGURE 6 Sample N47 Pyrex Powder in 50In-50Pb. Prepared  
by Manual Agitation of Charge with Tungsten Pestle  
in the Steel Container and Water Quenched 10.6x





### III. SUMMARY AND CONCLUSIONS

#### A. Processing Techniques

- Materials preparation techniques and metal-metal oxide systems processing methods have been developed which result in wetting of metal oxides by indium and indium-base alloys. The two most effective alloys are 50In-50Sn and 50In-50Pb. Two very different metal oxides have been successfully wet, aluminum oxide (crystalline) and a borosilicate glass. It is not believed that the bulk chemistry or form of the oxide are crucial to wetting and that other metal oxides would be wet by the indium alloys using the same basic procedure.
- Two factors appear to be vital to the achievement of wetting (1) thorough preparation of the metal oxides in highly oxidizing media, followed by drying or baking out of surface moisture, and (2) prepreparation of the metal-metal oxide systems with mechanical agitation or, more precisely, in the presence of some significant fluid shear flow of the metal fluid at the metal-metal oxide interface. The requirements appear to become more stringent as the metal oxide particle size decreases. Particle sizes smaller than  $177\mu\text{m}$  (80 mesh) could not be successfully wet, while uncleaned monolithic  $\text{Al}_2\text{O}_3$  was wet with only a gentle wiping action of the molten alloy (Figure 1).
- Samples were successfully processed by
  1. Wiping of the indium alloys on preheated monolithic oxide shapes with a heated tool (Figure 1).
  2. Manual mixing of the molten metal-metal oxide systems in a beaker followed by solidification in the beaker. (Sample N34, Figures 3a and 3b)
  3. Manual mixing of the molten metal-metal oxide systems in a beaker, followed by chill casting of the melt in a graphite mold. (Sample N43, Figure 4)
  4. Manual agitation of the molten metal-metal oxide systems in a stainless steel container with a tungsten pestle, followed by a water quench of the entire container. (Sample N47, Figure 6)
- All the particulate samples showed significant gravity segregation of the components. In the earth laboratory, this segregation could not be avoided, even by chill-casting of relative small samples. Low gravity processing can be expected to yield more homogeneous dispersions.

- Other techniques for metal-metal oxide processing, such as electromagnetic and ultrasonic stirring, were considered or pursued briefly but unsuccessfully, largely because of the inappropriateness of the available experimental apparatus for the specific experiments. It should not be concluded that these are not promising approaches to the processing of metal-metal oxide systems. An attempt was made to prepare a sample by vacuum baking of the metal powders with the objective of removing any remnant surface moisture or gases on the surface which might impede wetting. The attempt was unsuccessful, but it is believed that the associated mechanical mixing was too moderate in this case. Again, it should not be concluded that vacuum baking of the prepared powders is not a promising additional treatment to promote wetting.

#### B. Behavior of Metal-Metal Oxide Systems In Earth Laboratory Solidification Experiments

- While processing of model metal-metal oxide system exhibited variable results, as detailed in this report, some samples with oxide particle sizes of  $177\mu\text{m}$  (80 mesh) and greater were prepared by manual mixing of the pretreated materials. Several phenomena were observed which would be significant in the design of any proposed low gravity experiments with the model metal-metal oxide systems.
- Even under rapid quench conditions, gravity segregation of particles of this size is very fast, resulting in samples containing very high volume percent oxide content in the upper portions (Sample N47, Figure 6). When inverted, remelted, and resolidified under quiescent conditions, the expected resegmentation of the oxide particles did not occur, even though buoyancy forces and growth interface forces both acted in a direction which would be expected to force the particles to the other end of the samples. There was either interparticle bridging of the particles or locking because of the formation of matrix oxides in the matrix locally.
- At lower oxide volume loadings, with samples obtained by chill casting of a manually mixed system, inverted resolidification of the samples resulted in the expected resegmentation with fairly gentle agitation of the crucible. (Sample N41-2, Figure 5a)

- There is some evidence which suggests that, under certain solidification conditions, even metal oxide particles which have been wet by the matrix melt are rejected at the advancing solid-liquid interface (Sample N41-2, Figure 5a, in which cooling occurred from both the bottom and the sides). Attempts to perform an experiment in which the buoyancy and growth interface forces opposed each other were not successful. Growth interface forces must be considered in the design and interpretation of low gravity experiments, since they could produce segregation effects which are independent of the presence or absence of buoyancy forces.

#### IV. RECOMMENDATIONS

During the course of this program, it was agreed that the emphasis of the investigations should be placed on the development of techniques for producing metal-metal oxide systems and an understanding of their behavior in the earth laboratory. Near-term low gravity experiments which might be proposed for Phase 2 of this program would make use of existing low gravity experimental equipment or facilities which might require only minor modifications to adapt them for the metal-metal oxide systems.<sup>(16)</sup> The most suitable apparatus appeared to be that developed for the drop tower facility for the production of small bismuth-gallium alloys (having liquid immiscibility) by the TRW Systems Group.<sup>(3)</sup> The heating system is adequate, since these alloys have liquidus temperatures similar to those of the matrix alloys investigated in this program. The cooling system is more than adequate, since the solidus-liquidus gap is much greater for the bismuth-gallium system investigated than it is for the indium-based alloys. It was recognized that heating of the sample in the TRW apparatus is accomplished under static, 1-g conditions which would lead to an initially segregated molten metal-metal oxide system. Modifications of the TRW apparatus were suggested which would make it suitable for low gravity experiments with metal-metal oxide systems. The primary modifications would be

1. Provision for rapid inversion of the sample container by 180° immediately prior to or during the first second of drop.
2. Incorporation of permanent magnet around the sample container to damp out the internal sample fluid flow which would be caused by the rapid 180° inversion.

Based on the results of the investigations during Phase 1 of this program, the low gravity experiment outlined above for Phase 2 is not recommended. The bases for this conclusion are:

1. The oxide bridging, agglomeration, or locking phenomenon which has to this point prevented expected gravity re-segregation in the earth laboratory without an appropriate amount of capsule agitation.
2. The difficulty of producing low oxide volume percent metal-metal oxide samples in which the oxide is wet. Such samples might be processed by faster quenching of melts in which finer oxide particle sizes are incorporated. This might also help obviate the oxide particle locking problems.
3. The dewetting of the oxide particles and their rejection at solid-liquid interfaces was observed. The particle size, volume fraction of the oxide powder, and solidification parameters upon remelt are not at this time sufficiently well defined to design a meaningful low gravity experiment.

Prior to the design and implementation of low gravity experiments for metal-metal oxide systems, it is recommended that added work be carried out in the earth laboratory to further refine the sample preparation procedures and the subsequent processing conditions which will yield that greatest amount of information relative to differences between earth and low gravity processing. The recommended approaches are:

1. Improvement in sample preparation procedures, with particular reference to the enhancement of wetting of smaller size oxide particles by the inclusion of a vacuum bake-out procedure. The Arthur D. Little, Inc., M.P. Furnace is suited to this, (with the capability of maintaining vacuum of  $5-8 \times 10^{-5}$  mm Hg) with modifications to enhance mechanical agitation of the system. Such modifications would be made on the upper head by increasing its rotational velocity capabilities and design of a more efficient mixing tool. Alternatively, it may be more appropriate to introduce either acoustic or ultrasonic energy into the upper head to obtain mechanical agitation in the vertical mode. A cold plate would be incorporated into the furnace to enhance quenching by lowering of the sample container down onto it by means of the bottom head of the furnace. Means for monitoring the temperature of the sample would also be incorporated.
2. Modification of sample preparation procedures using mechanical agitation techniques by redesign of the metal sample container to permit extended mixing in the molten state and quenching on the various available mechanical agitation equipment. This equipment can be used to prepare samples directly or to further prepare samples processed in the vacuum apparatus.
3. Conduct four basic types of experiments in the earth laboratory to define the subsequent remelt behavior of the prepared metal-metal oxide systems. These are:
  - Particles at the bottom of the sample, solidification upon remelt vertically upwards.
  - Particles at the bottom of the sample, solidification upon remelt vertically downwards.
  - Particles at the top of the sample, solidification upon remelt vertically upwards.
  - Particles at the top of the sample, solidification upon remelt vertically downwards.

These experiments would serve to further define the sample characteristics and experimental design and parameters required for a meaningful low gravity experiment on the metal-metal oxide systems.

## V. REFERENCES

1. "Apollo 14 Composite Casting Demonstration," Final Report, Report No. TM X-64641, George C. Marshall Space Flight Center, Alabama, October 1971.
2. "Apollo 14 Composite Casting Demonstration," Final Report, Contract No. NAS8-26637, Arthur D. Little, Inc., Cambridge, Mass., August 1971.
3. "Experimental Development of Processes to Produce Homogenized Alloys of Immiscible Metals," Final Report, Phase III, No. 18677-6019-RU-00, Contract No. NAS8-27805, TRW Systems Group, Redondo Beach, Cal.
4. "Space Processing of Composite Materials," Progress Report No. 3, Contract No. NAS8-29620, Convair Aerospace Division of General Dynamics, San Diego, Cal., August 20, 1973.
5. D.R. Uhlmann and B. Chalmers, "Interaction Between Particles and a Solid-Liquid Interface," J. Appl. Phys., 35(10), 2986-2993, October 1964.
6. G.F. Bolling and J. Cissé, "A Theory for the Interaction of Particles with a Solidifying Front," J. Crystal Growth, 10, 56-66 (1971).
7. J. Cissé and G. F. Bolling, "A Study of the Trapping and Rejection of Insoluble Particles During the Freezing of Water," J. Crystal Growth 10, 67-76 (1971).
8. H. Manko, Solders and Soldering Materials, Design, Production and Analysis for Reliable Bonding, (McGraw Hill Book Co., 1964).
9. W.H. Konl, Handbook of Materials and Techniques for Vacuum Devices, (Reinhold Publishing Co., New York, 1967).
10. Product Literature, Indium Corporation of America, 1676 Lincoln Ave., P.O. Box 269, Utica, New York.
11. Handbook of Chemistry and Physics, 53rd ed. CRC Press, Division of the Chemical Rubber Co., 1973.
12. R.P. Elliot, Constitution of Binary Alloys, First Supplement, McGraw-Hill, New York, New York, 1965.
13. R.B. Belser, "Frictional Adhesion of Metal to Glass, Quartz and Ceramic Surfaces, Rev. Sci. Inst. 25, 862-864, September 1954.
14. J. C. McGuire, "New Method for Soft Soldering Metals and Ceramics," Rev. Sci. Inst. 26, 893, September 1955.

15. "Study on Processing Immiscible Materials in Zero Gravity," Monthly Progress Report No. 11, Contract No. NAS8-28267, TRW Systems Group, Redondo Beach, Cal., September 18, 1973.
16. "Development of Techniques for Processing Metal-Metal Oxide Systems," Monthly Progress Report No. 5, Contract No. NAS8-29145, Arthur D. Little, Inc., Cambridge, Massachusetts, April 4, 1973.